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Polyaniline based electrodes for electrochemical supercapacitor: Synergistic effect of silver, activated carbon and polyaniline

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ABSTRACT

The composite thin films of Silver–activated carbon/polyaniline (Ag–AC/PANI) have been deposited on stainless steel substrates by a facile dip coating technique. The formation of Ag–AC/PANI electrode is analyzed by Fourier transform infrared, Fourier transform-Raman and X-ray photoelectron spectroscopy techniques. Field Emission Scanning Electron Microscopy revealed the presence of Ag nanoparticles on the porous spongy background of PANI. The highest specific capacitance of 567 $\mathrm{Fg^{-1}}$at 5 $\mathrm{mV\,s^{-1}}$ and energy density of 86.30 $\mathrm{W\,h\,kg^{-1}}$ at 1 $\mathrm{mA\,cm^{-2}}$ is observed for the Ag–AC/PANI indicating positive synergistic effect of silver, activated carbon and PANI. In which silver nanoparticles help in improving the electronic conductivity and activated carbon enhances the electrochemical stability of the PANI electrodes.

1. Introduction

Supercapacitors, also known as electrochemical capacitors or ultracapacitors have attracted much attention because of their pulse power supply, long cycle life, simple principle and high dynamic of charge propagation [1,2]. According to the charge storage mechanism supercapacitors can be divided into two subclasses: 1. Electrical double layer capacitor (EDLC) in which the capacitance arises from the charge separation at the electrode–electrolyte interface and 2. Pseudocapacitors in which the pseudocapacitance arises from faradaic reaction occurring at the electrode–electrolyte interface. They can store much more energy than conventional capacitors and offer higher power density than batteries. Batteries are widely used for energy storage in industrial and consumer electronics devices because of their high energy density but are limited in their power density. When a battery is charged or discharged, the redox reactions change the molecular or crystalline structure of the electrode materials, which often affects their stability so batteries generally must be replaced after several thousand charge–discharge cycles. Unlike batteries, in pseudocapacitors ions simply cling to the atomic structure of an electrode. This faradaic energy storage with only fast redox reactions makes charging and discharging much faster than batteries [3]. When high power is required in battery operated devices (i.e. in pulse applications), the combination of the supercapacitor connected in parallel to the battery gives the advantages of both, enhancing the performance of the battery and extending its life, exploiting the batteries to its maximum potential. The main three categories of electrode materials for electrochemical capacitors are carbon materials such as carbon nanotubes, Activated carbons (AC), transition metal oxides like MnO_2, RuO_2 and electronically conducting polymers (CP) viz., Polyaniline (PANI), polypyrrole [4–10]. Among the above, the conducting polymers offer the advantages of lower cost in comparison with metal oxides and high charge density in contrast to carbon materials.

PANI is one of the most promising materials which is frequently used as electrode material for supercapacitor due to its properties such as easy synthesis, controllable electric conductivity, chemical stability and three oxidation states (Leucoemeraldine, Emeraldine and Pernigraniline) which contribute to its high specific capacitance [11–15]. The oxidation and reduction processes are accompanied by doping (intercalation) and dedoping (deintercalation) of counter-anions respectively. Since these processes are reversible, charge storage in PANI is facilitated to yield a pseudocapacitance (C_ϕ) behavior. Additionally, separation of charges takes place at

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the PANI electrolyte interface and this gives rise to the existence of double layer capacitance (C_{dl}) Thus, the total capacitance, $C_t = C_{dl} + C_{\phi}$ [10]. However the Ag–AC/PANI nanocomposite films investigated in this study exhibit porous and spongy morphology. Thus an electrolyte penetrates into the nanocomposites to manifest 3-D electrode–electrolyte interface to augment C_{ϕ}. The excellent electrode required for the supercapacitor consists of good electronic conductivity, electrochemical stability and high surface area. The main drawback of using PANI as supercapacitor electrode is mainly concerned with their low cycle life because during the doping/dedoping process (insertion/deinsertion of counter ions) undergoes swelling and shrinkage leading to mechanical degradation of the electrodes [16,17]. To overcome this problem, research has focused on synthesizing PANI/carbon based materials (such as AC, Carbon nanotubes, and Graphene) and PANI/ Metal oxides (such as RuO_2, and MnO_2) composite electrodes [18–22]. The electronic conductivity of green protonated emeraldine form of PANI is lower than that of metals [23]. So, one of the challenging issues in development of high performance supercapacitor is to improve its electronic conductivity of the PANI electrode which is reversibly controlled both by the charge transfer doping and by protonation. Extensive research work has been focused on enhancing electronic conduction of the electrodes by using metal doping [24–27].

We have reported on Mn doped PANI and Ag doped PANI electrodes for supercapacitor with specific capacitances of $\sim$474 Fg^{-1} and 512 Fg^{-1} respectively [28,29]. The enhanced electron transfer in the Ag/PANI system is attributed to the charge hopping through the metallic conductor Ag nanoparticles that mediate the effective charge migration through the PANI. However, there have been a limited number of studies on the effect of metal incorporation between carbon materials and CP on the electrochemical properties of carbon materials/CP nanocomposites [30–33] .

Therefore in the present investigation, firstly AC/PANI composite was prepared by using in situ chemical oxidative polymerization of the corresponding aniline monomer and silver nanoparticles incorporated into AC/PANI composite. The structural and morphological properties of PANI, Ag–PANI, AC/PANI and Ag–AC/PANI are investigated. The effect of Ag nanoparticles on electrochemical performance such as specific capacitance, current density and electrochemical stability of the AC/PANI composite electrode is discussed.

2. Experimental details

Ag–AC/PANI films were chemically synthesized by adopting two step processes: initially the AC/PANI composite was prepared by using an in situ polymerization method. Briefly, the aniline monomer was first mixed with AC in 1 M HCl by ultrasonication to form a homogeneous suspension. Ammonium persulphate (APS) was dissolved separately in 1.0 M HCl. Then APS was added to this mixture to obtain the homogeneous composite of AC/PANI. Afterward, optimized quantity (1.2 wt.%) of silver nitrate ($AgNO_3$) was dissolved in the AC/PANI solution. When $AgNO_3$ added into the solution then protonation takes place and PANI gets oxidized and metallic silver was produced with nitric acid as a byproduct. To obtain the uniform distribution of Ag ions in the AC/PANI solution, the mixture was ultrasonicated for 30 min. Uniform depositions of Ag–AC/PANI films were obtained on stainless steel substrates by dip coating technique. The solution was kept under constant stirring for proper dispersion of Ag in AC/PANI throughout the film deposition process. The size of stainless steel samples was 2 cm × 1 cm approximately. The thickness of the films was measured by using Ambios XP-1 surface profiler which is about 880 nm. The mass of active material ($\sim$0.3 mg) was calculated from weight difference between the weight of substrate before deposition and weight of the substrate after deposition. PANI film was prepared by without addition of AC and $AgNO_3$ whereas Ag–PANI and AC/PANI films were prepared by without addition of AC and $AgNO_3$ respectively.

Infrared (IR) spectroscopy was used to confirm the formation of PANI in which the powdered material collected from the deposited film was characterized by infrared spectrometer (Perkin–Elmer, model 783, USA). Raman studies were conducted using Bruker make FT-Raman spectrometer. The Raman spectra were recorded by a laser radiation at an excitation wavelength of 1064 nm. X-ray photoelectron spectra were recorded by using XPS, VG Multilab 2000, Thermo VG Scientific, UK, for phase evaluation. The surface morphology of the films was examined by analyzing the Field emission scanning electron microscope (FE-SEM), JEOL JSM JSM-6500F equipped with an energy dispersive X-ray spectrometer (EDS). The electrochemical measurements were performed in an electrolyte of 1.0 M H_2SO_4 in a conventional three electrode arrangement comprising graphite counter electrode and saturated calomel electrode (SCE) serving as the reference electrode, using scanning potentiostat (model-CHI-400A) CH Instrument, USA. The charge–discharge and electrochemical impedance spectroscopy (EIS) experiment is carried out in the three electrode cell consisting of platinum as counter electrode and SCE as reference using Wonatech WMPG 1000-potentiostat- Galvanostat.

3. Results and discussion

All the samples were subjected to the structural, optical, morphological and electrochemical characterization.

Fig. 1(a–e) shows the FTIR spectra of the powders collected from AC, PANI, Ag–PANI, AC/PANI and Ag–AC/PANI samples over 900–1900 cm^{-1}. The FTIR spectrum for AC is as shown in Fig. 1(a) there are four peaks at 1612, 1163, 1120 and 1021 cm^{-1}. The PANI (Fig. 1(b)) spectrum consists of four distinct peaks; at 1560, 1492, 1304 and 1131 cm^{-1}. The bands are assigned to the N═Q═N stretching, N—B—N stretching (where Q & B denotes the quinoid & Benzenoid), N—H bending and —N═ vibration respectively, which are similar to those obtained by Li et al. [34].

The samples Ag–PANI, AC/PANI and Ag–AC/PANI exhibit all the peaks corresponding to PANI. The intensity of peaks for Ag-PANI and Ag–AC/PANI decreases as compared to PANI sample due to the presence of Ag nanoparticles in the polymer matrix which is consistent with the observation of Khanna et al. [35].The peaks

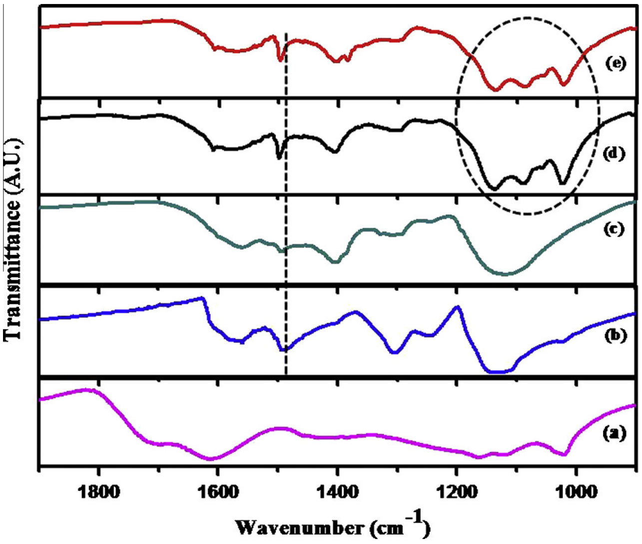

Fig. 1. FT-IR transmittance spectra of the (a) AC, (b) PANI, (c) Ag–PANI, (d) AC/PANI and (e) Ag–AC/PANI samples recorded in the wavenumber range of 900–1900 cm^{-1}.